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(54) PROCESS FOR THE MANUFACTURE OF TECHNICAL  
AND MEDICINAL WHITE OILS

- (71) We, BASF AKTIENGESSELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following Statement:—
- The present invention relates to novel processes for the manufacture of technical and medicinal white oils.
- White oils are highly refined petroleum fractions which are free from oxygen-containing, nitrogen-containing and sulphur-containing compounds and, depending on their use, contain either small amounts of aromatics (technical white oils) or virtually no aromatics (medicinal white oils). Technical white oils have a variety of applications as carriers for insecticides and herbicides and also as ingredients in printing inks for textiles. Medicinal white oils are mainly used in the manufacture of cosmetics and medicinal preparations. Medicinal white oils are also used as lubricants in food-processing machines. In these latter applications it is important for the white oils to be tasteless, odourless, colourless and substantially inert, that is, in particular, they should be free from toxic substances such as aromatics.
- Prior art processes for the manufacture of white oils start from suitable petroleum fractions which are refined either directly or after partial removal of the aromatics by solvent extraction using, for example, furfural, SO<sub>2</sub>, phenol, or highly concentrated sulphuric acid or oleum. In such processes, the impurities present in the oil, for example compounds containing sulphur, nitrogen and oxygen, and also the aromatics are removed. In order to remove the last traces of aromatics and impurities from the refined oil, particularly the sulphonates formed during the treatment with sulphuric acid, the raffinate is neutralized and then usually subjected to treatment with bleaching earth or extraction with alcohols. For information on the refining of petroleum fractions with sulphuric acid see B. Riediger, "Die Verarbeitung des Erdöls", Springer-Verlag, 1971, pp. 655 et seq., particularly p. 657, 3rd paragraph. In the treatment of petroleum products with sulphuric acid, high losses of yield due to the formation of aromatic sulphonic acids must be accepted. Furthermore, the removal of the acid tars produced involves considerable environmental problems. Also the refining of highly viscous petroleum fractions with sulphuric acid produces great difficulties arising from emulsion and settling problems. Despite these disadvantages, new processes for the manufacture of white oils have recently been proposed (cf. U.S. Patent 3,553,107) in which an initial catalytic stage is followed by further treatments with fuming sulphuric acid and alcohol extraction.
- However, multi-stage catalytic refining processes for the manufacture of white oils have been proposed in order to avoid treatment with sulphuric acid. For example, German Published Application 1,645,791 describes a two-stage catalytic process in which a low-aromatics petroleum fraction is hydrogenated in a first catalytic stage in contact with a sulphur-tolerant hydrogenation catalyst and in a second stage in contact with a catalyst containing a noble metal. In German published Application 2,050,908 a two-stage catalytic process for the manufacture of medicinal white oils from solvent raffinates is described, in which sulphur-tolerant catalysts are again used in the first stage, whilst complex catalysts of a metal in group VIII of the Periodic Table are used in the second stage.
- The main problem encountered in the manufacture of white oils, particularly medicinal white oils, is the extremely low maximum permissible residual content of aromatics. It is thus important to find a sufficiently active hydrogenation catalyst, since the hydrogenation of aromatics is greatly hampered, for kinetic reasons, by the high molecular weight of the starting products and the presence of polycondensed aromatic

compounds. In order to produce standard white oils by catalytic hydrogenation, it has previously been necessary to start from low-aromatics petroleum, the so-called naphthen-base oils, even when using noble metal catalysts (cf. German Published Application 1,654,792). When catalysts not containing noble metals are used, it is necessary to reduce the aromatics content of the petroleum fraction to be hydrogenated to preferably less than 5% by solvent extraction (cf. German Published Application 2,050,908).

Another problem encountered in the hydrogenation of starting products for white oil which contain a higher percentage of aromatics is the heat of hydrogenation which is generated during the hydrogenation of the aromatics. It is imperative to restrict the rise in temperature during hydrogenation by installing quenching zones in the reactor, since at a given pressure an undue rise in temperature would shift the thermodynamic equilibrium towards dehydrogenation to form aromatics. However, the use of quenching zones greatly increases the cost of the plant.

We have found that technical white oils may be manufactured in a single-stage catalytic hydrogenation process, in which the aromatics are substantially hydrogenated together with removal of the sulphur-containing, oxygen-containing and nitrogen-containing compounds, if the catalytic hydrogenation is carried out in the presence of a supported catalyst which contains a particular amount of molybdenum together with nickel and phosphoric acid and which has been prepared by impregnation of the support with a hereinafter described solution.

We have also found that medicinal white oils may be manufactured from the resulting technical white oils, or other product of which the aromatic content has partially been hydrogenated, by completing the hydrogenation of the residual aromatics in a second catalytic stage employing a metallic nickel or other base catalyst.

Accordingly, in one aspect, the invention provides a process for the manufacture of a technical white oil which process comprises subjecting to catalytic hydrogenation a petroleum fraction which boils in the range 200° to 550°C and which contains aromatic compounds together with nitrogen-containing, oxygen-containing, and sulphur-containing compounds and which may or may not have been subjected to solvent extraction, the catalytic hydrogenation being carried out in a single stage at superatmospheric pressure and elevated temperature in the presence of a sulphurised catalyst which contains molybdenum in an amount of from 10% to 15% by weight (measured as MoO<sub>3</sub>) together with nickel and phosphoric acid and which has been prepared by impregnating a catalyst

support with a solution containing Ni<sup>2+</sup> cations, MoO<sub>4</sub><sup>2-</sup> anions and PO<sub>4</sub><sup>3-</sup> anions.

As mentioned above, the solution used to impregnate the support contains the anions PO<sub>4</sub><sup>3-</sup> and MoO<sub>4</sub><sup>2-</sup> together with Ni<sup>2+</sup> cations. Under normal circumstances, such a solution will be a solution of soluble nickel compounds of phosphorous/molybdenum heteropolyacid anions formed by interaction of the anions mentioned above. It is to be understood that processes carried out using a catalyst prepared from such a solution are included within the scope of the invention.

In a second aspect, the invention provides a process for the manufacture of a medicinal white oil which process comprises subjecting to catalytic hydrogenation a petroleum fraction which boils in the range 200° to 550°C and which contains aromatic compounds together with nitrogen-containing, oxygen-containing and sulphur-containing compounds and which may or may not have been subjected to solvent extraction, the catalytic hydrogenation being carried out in two stages of which the first hydrogenation stage is carried out at superatmospheric pressure and elevated temperature and effects hydrogenation of the nitrogen-containing, oxygen-containing and sulphur-containing compounds and a portion of the aromatic compounds and is carried out in the presence of a catalyst as defined above, and of which the second hydrogenation stage effects completion of the hydrogenation in contact with a base metal catalyst.

Suitable starting products for the manufacture of white oils of technical and medicinal grades are oils boiling in the range 200° to 550°C, for example gas oil fractions boiling at from 220°C to 340°C, spindle oil fractions or other lubricating oil fractions. Higher-boiling starting products generally require more stringent refining conditions. The aromatics content of the crude oils is not particularly critical, since the aromatics are substantially removed by hydrogenation in the first stage of the process. Only in very special cases where the aromatics content of the crude oil is abnormally high, for example in the range of 30% or more, can it be advantageous to remove some of the aromatics by extraction prior to carrying out the present process.

In the first catalytic refining stage use preferably is made of a sulphidic catalyst which, in the oxide state, contains from 3 to 6% of nickel oxide, from 10 to 15% of molybdenum oxide and from 3 to 6% of o-phosphoric acid on a support, these percentages being based on the total weight of the catalyst. The preferred support is one containing alumina, particularly  $\gamma$ -aluminium oxide. For example, the support consists of from 100 to 95% by weight of  $\gamma$ -aluminium oxide and from 0 to 5% by weight of SiO<sub>2</sub>.

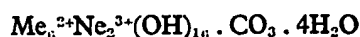
The manufacture of the catalyst differs from the usual methods of manufacturing, say, catalysts containing cobalt and molybdenum or nickel and molybdenum or nickel and tungsten in that the support is impregnated with a solution of nickel molybdate in phosphoric acid, this being described in detail in Example 1 below.

This specific catalyst containing nickel, molybdenum and phosphoric acid is used to hydrogenate the petroleum fraction conveniently under the following conditions: pressure from 30 to 200 and preferably from 75 to 200 atmospheres; temperature from 250° to 370°C and preferably from 300° to 350°C; gas/oil ratio from 0.1 to 1.0 m<sup>3</sup> of hydrogen (STP) per kilogram of oil; space velocity 0.15 to 1.0 kg of oil per litre of catalyst per hour.

The use of the said catalyst in the refining of crude products for making white oils has a great advantage over the use of conventional refining catalysts, since it hydrogenates very much more aromatic material for a given degree of desulphurization. It is thus possible to manufacture technical white oils, printing ink oils or carrier oils for insecticides in a single stage (cf. Examples 3 and 4). In the two-stage method of producing medicinal white oils, the performance required of the second hydrogenation stage is diminished.

By distributing the heat of hydrogenation over two hydrogenation stages, it is possible to remove this heat in a more economical manner without the use of quenching zones in the reactor of the second stage. Furthermore, the entire process can be carried out under milder conditions, e.g. at lower temperatures and pressures. This means that cracking of the crude material is substantially obviated and undue reductions in viscosity are avoided. Furthermore, only a relatively small amount of aromatics needs to be removed in preliminary solvent extraction operation, if carried out.

Catalysts used in the second catalytic refining stage of medicinal white oil production are suitably those available from precatalysts obtained by precipitation of appropriate compounds from aqueous solution and having the general formula:



where Me<sup>2+</sup> is Fe, Co, Ni or Mg and Ne<sup>3+</sup> is Al or Cr. The manufacture of such catalysts is described in German Published Application 2,024,282.

We prefer to use catalysts available from the precatalyst



When this material is compressed, calcined

above 350°C and reduced in a stream of hydrogen, there is obtained a catalyst which is suitable for fixed-bed reaction and which contains about 64% by weight of nickel. Due to its high content of metal and the very fine degree of subdivision of the metal it is extremely active for hydrogenation reactions. The fineness of the metal also reduces the tendency of the metal to recrystallize, which means that the exceptionally high activity of the catalyst is retained for a comparatively long period. X-ray examinations have shown that after reduction nickel is present in an average crystallite size of the order of 20 to 60 Å (for a definition of the average crystallite size see Kluge-Alexander "X-ray Reflection Procedures", John Wiley and Sons, 1954 pp. 511 et seq.). We prefer to use catalysts containing nickel having an average crystallite size of from 20 to 50 Å. Due to the high activity of undiluted catalysts it is possible to use catalysts having reduced nickel contents of as low as 10% or less, since the activity of such catalysts is adequate for most hydrogenation reactions. In the manufacture of white oils, catalysts having nickel contents of between 20 to 64% are preferred. Dilution of the nickel in the precatalyst is effected by means of active diluents. By "active diluents" we mean aluminium oxides or aluminium oxide/silicon dioxide mixtures of large surface area which are themselves catalytically active on account of their surface properties and thus increase the activity of the NiO/Al<sub>2</sub>O<sub>3</sub> system obtained from the precatalyst. The activity of the catalyst may also be modified in known manner by introducing MgO, CaO, ZnO, B<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> in amounts of from 1 to 10% by weight.

Particularly suitable large-area aluminium oxides can be obtained by precipitating aluminium oxide hydrates from aqueous solutions containing aluminium salts. The solutions used as starting materials may be acid aluminium salt solutions or aluminate solutions and from these there may be produced, in the first case using alkaline solutions such as ammonia and in the second case using acids such as CO<sub>2</sub> or acid aluminium salt solutions, the well-known intermediates of oxide hydrates such as bayerite, hydragillite or boehmite, from which γ- or η-aluminium oxides may be prepared by known methods.

The second catalytic hydrogenation stage in medicinal white oil production is conveniently carried out under the following conditions: pressure from 50 to 250 and preferably from 100 to 200 atmospheres; temperature from 200 to 350° and preferably from 220 to 330°C; gas/oil ratio 0.1 to 1.0 m<sup>3</sup> of hydrogen (STP) per kg of oil; space velocity 0.15 to 2.0 kg of oil per litre of catalyst per hour.

The following Examples, in which all parts

and percentages are measured on a weight basis, serve to illustrate the invention. Examples 1 and 2 describe the manufacture of the catalysts used in stage 1 (catalyst C) and in stage 2 (catalyst D) in the process of the invention. The Examples include comparative experiments which demonstrate the superiority of these catalysts over prior art catalysts. Examples 3 and 4 illustrate the use of the catalyst described in Example 1 and 2 in the manufacture of technical white oils (Examples 3 and 4, single-stage operation) or of medicinal white oils (Example 4, two-stage operation).

#### Example 1

This Example describes the preparation of the catalyst containing nickel, molybdenum and phosphoric acid for use in the first refining stage (catalyst C). This Example also contains a comparison of the activity of this catalyst with that of a sulphur-tolerant cobalt/molybdenum (catalyst A) or nickel/molybdenum catalyst (catalyst B) produced in known manner. The catalysts were manufactured as follows and sulphurized in known manner before use.

Catalyst A (5% of cobalt oxide and 13.0% of  $\text{MoO}_3$ )

From an  $\text{Al}_2(\text{SO}_4)_3$  solution (7.5% of  $\text{Al}_2\text{O}_3$ ) an aluminium oxide hydrate was precipitated with 25%  $\text{NH}_4\text{OH}$  at pH of 6.5 and a temperature of  $85^\circ\text{C}$ , and the precipitate was washed free of sulphate with 0.25%  $(\text{NH}_4)_2\text{CO}_3$  solution and dried at  $120^\circ\text{C}$ . 230 g (163 g of  $\text{Al}_2\text{O}_3$ ) of this aluminium oxide were mixed with 38.8 g of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (dissolved in 50 ml of water) and 25.8 g of  $\text{MoO}_3$  (dissolved in 25 ml of 25% ammonia) in a kneader therein for 30 minutes. The composition was extruded to pellets having a diameter of 1.5 mm, dried for 12 hours at  $150^\circ\text{C}$  and then calcined for 4 hours at  $500^\circ\text{C}$ . The finished catalyst contained 5% of cobalt oxide and 13% of molybdenum oxide supported on  $\gamma$ -aluminium oxide.

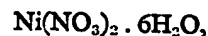
Catalyst B (5% of  $\text{NiO}$  and 13%  $\text{MoO}_3$ )

This catalyst B was prepared by extruding the aluminium oxide used in the preparation of catalyst A to pellets having a diameter of 1.5 mm after the aluminium oxide had been calcined at  $500^\circ\text{C}$ . 1,000 g of these pellets were impregnated with a solution of nickel molybdate in ammonia at such a rate that the final catalyst had, after calcination, 5% of nickel oxide and 13% of molybdenum oxide.

Catalyst C

1,000 g of the  $\gamma$ -aluminium oxide extrudates having a diameter of 1.5 mm and

calcined at  $500^\circ\text{C}$  as used in the manufacture of catalyst B were sprayed with 755 g of an aqueous solution containing 22.1% of  $\text{MoO}_3$ , 8.5% of  $\text{NiO}$  and 6.8% of phosphoric acid, by weight. This solution was prepared by fusing  $\text{MoO}_3$  sublimate by heating with the calculated amount of an orthophosphoric acid solution. This solution was added to the required amount of



to give a clear solution. The impregnated extrudates were dried for 12 hours at  $120^\circ\text{C}$  and then calcined for 2 hours at  $350^\circ\text{C}$ . The final catalyst contained 5% of  $\text{NiO}$ , 13% of  $\text{MoO}_3$  and 4% of  $\text{H}_3\text{PO}_4$ .

For the purposes of comparing the activities of these catalysts A, B and C, 100 ml of each of the catalysts, previously sulphurized, were placed in a testing apparatus and were treated with 1 kg of benzene per litre of catalyst per hour at a temperature of  $350^\circ\text{C}$  and a hydrogen partial pressure of 15 atmospheres. The sulphur content in the benzene was 10 ppm and was reduced by all three catalysts to a value of less than 0.5 ppm. The content of cyclohexane in the product was taken as the measure of hydrogenation activity. The results are listed in Table 1 below.

TABLE 1

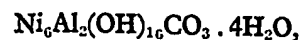
| Catalyst | Content of cyclohexane in product |
|----------|-----------------------------------|
| A        | 2.55% w/w                         |
| B        | 3.07% w/w                         |
| C        | 5.60% w/w                         |

These tests show that the nickel/molybdenum catalyst containing phosphoric acid is superior to both the cobalt/molybdenum catalyst A and the phosphoric acid-free nickel/molybdenum impregnated catalyst B.

#### Example 2

This Example describes the preparation of the nickel catalyst to be used in the second hydrogenation stage, for illustration a catalyst containing about 30% by weight of nickel.

To effect precipitation of the precatalyst



the following solutions 1 and 2 were prepared.

#### Solution 1

55.84 kg of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 24.01 kg of  $\text{Al}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$  were dissolved in water giving a final solution volume of 128 litres.

## Solution 2

30.54 kg of  $\text{Na}_2\text{CO}_3$  were dissolved in water giving a final solution volume of 144 litres.

- 5 Solutions 1 and 2 were heated separately at  $80^\circ\text{C}$  and added to 40 litres of water at the same temperature with vigorous stirring. The feed rates of solutions 1 and 2 were regulated so as to maintain a pH of 8 during precipitation of the hydroxide carbonate. The precipitate was washed free of nitrate and alkalis and then dried at  $110^\circ\text{C}$ . 100 g of the dried hydroxide carbonate were mixed with 84 g of the  $\gamma$ -aluminium oxide as prepared in Example 1, mixing being carried out in a kneader with the addition of water. After a kneading period of 30 minutes, the compositions were extruded to pellets having a diameter of 1.5 mm. The pellets were dried and calcined for 5 hours at  $500^\circ\text{C}$ . After reduction with hydrogen at  $450^\circ\text{C}$ , there was obtained a catalyst containing 30% by weight of nickel. A sample of the catalyst was subjected to X-ray examination, which showed nickel crystallites having an average size of 40 Å. Due to the extremely fine state of subdivision of the nickel, this catalyst shows much higher activity than conventional nickel catalysts. Its activity in the hydrogenation of aromatics is surprisingly higher than that of platinum catalysts (cf. Table 2 below). Another advantage of catalyst thus produced is that they can be used at temperatures above  $400^\circ\text{C}$  without any reduction in their activity due to recrystallisation. Both Raney nickel catalysts and platinum catalysts (Adams) show considerable losses in activity at these temperatures, mainly due to recrystallisation.
- 40 The superiority of the above nickel catalyst over conventional hydrogenation catalysts is illustrated below with reference to a desulphurized naphtha (Table 2) and a higher-boiling fraction (refining of a technical white oil to a medicinal white oil, Table 3).
- 45 A desulphurized naphtha boiling in the range  $38^\circ$  to  $120^\circ\text{C}$  and having a content of 2.56% w/w of benzene, 1.70% w/w of toluene and 0.35% w/w of xylenes was hydrogenated in different tests each using 100 ml of the following catalysts:

## Catalyst D

Nickel catalyst as described in Example 2 and containing 30% by weight of nickel.

## 55 Catalyst E

- Platinum catalyst containing 0.6% w/w of platinum supported on a sulphate-free  $\alpha$ -aluminium oxide prepared by impregnating the support with a solution of hexachloroplatinate, drying and reducing with hydrogen at  $450^\circ\text{C}$ .

The test conditions and the results are listed in Table 2 below:

TABLE 2

| Catalyst                         | D   | E   | D   | E    |    |
|----------------------------------|-----|-----|-----|------|----|
| pressure (atm)                   | 30  | 30  | 15  | 15   | 65 |
| temperature ( $^\circ\text{C}$ ) | 290 | 290 | 270 | 270  |    |
| throughput (g/hr)                | 200 | 200 | 100 | 100  |    |
| aromatics in raffinate (ppm)     | 200 | 700 | 400 | 2000 | 70 |

It is seen from Table 2 that the nickel catalyst used in the present invention is from 2 to 3 times more active in the hydrogenation of aromatics than the noble metal catalyst.

Table 3 lists the test conditions and the results obtained in the hydrogenation of a technical white oil to a medicinal white oil in tests using the said nickel catalyst (catalyst D) and a prior art platinum catalyst (catalyst E), 100 ml of these catalysts being used in each test.

TABLE 3

| Catalyst                         | D   | D   | E   |    |
|----------------------------------|-----|-----|-----|----|
| pressure (atm)                   | 200 | 200 | 200 | 85 |
| temperature ( $^\circ\text{C}$ ) | 280 | 310 | 310 |    |
| throughput (g/hr)                | 150 | 150 | 150 |    |
| light absorption of raffinate at |     |     |     |    |
| 275 nm (DAB 7 limit 0.8)         | 0.3 | 0.2 | 1.0 | 90 |
| 295 nm (DAB 7 limit 0.4)         | 0.2 | 0.1 | 0.6 |    |
| 300 nm (DAB 7 limit 0.3)         | 0.1 | 0.1 | 0.5 | 95 |

The light absorption of the raffinate at 275, 295 and 300 nm is taken as the measure of the aromatics content as specified by DAB 7 (German Pharmacopoeia 7th Edition). From Table 3 it is seen that when the platinum catalyst E is used, the minimum values of ultraviolet light absorption, as specified by DAB 7, are not achieved, whereas use of the nickel catalyst D even at lower working temperatures satisfies the requirements for medicinal white oils.

## Example 3

For the manufacture of a printing ink oil or a carrier oil for insecticides, a gas oil boiling in the range  $235^\circ$  to  $320^\circ\text{C}$  and having a density (at  $15^\circ\text{C}$ ) of 0.835 g/l and a sulphur content of 0.31% is hydrogenated in contact with the catalyst C described in Example 1 at a total pressure of 75 atmospheres, a temperature of  $346^\circ\text{C}$  a space velocity of 0.25 kg of oil per litre of catalyst per hour and a hydrogen/oil ratio of 0.53  $\text{m}^3$  of hydrogen (STP) per kg of oil.

Table 4 compares the properties of the starting oil with those of the product.

120

TABLE 4

|                          | Gas oil | Product |
|--------------------------|---------|---------|
| density at 15°C (g/l)    | 0.835   | 0.819   |
| bromine number           |         |         |
| 5 (g/100 g)              | 1.6     | 0.2     |
| oxygen content (ppm)     | 150     | 0       |
| sulphur content (ppm)    | 3100    | 0.6     |
| nitrogen content (ppm)   | 200     | 2.0     |
| aniline point (°C)       | 73.8    | 81.1    |
| 10 mononuclear aromatics |         |         |
| (% w/w)                  | 14.1    | 3.9     |
| dinuclear aromatics      |         |         |
| (% w/w)                  | 7.4     | 0.03    |

Despite the relatively mild working conditions, the sulphur compounds were decomposed to give a final sulphur content of less

than 1 ppm and the aromatics content was reduced from 21.5% to 3.93%, by weight.

## Example 4

For the manufacture of a technical and a medicinal white oil, a mineral oil fraction boiling in the range 360° to 480°C and having a density of 0.868 (at 20°C), a viscosity of 25.32 centistokes (at 15°C), an oxygen content of 120 ppm, a sulphur content of 0.37% and a nitrogen content of 0.031% were used as starting materials. The aromatics content was 11.6%, by weight. In a first stage, this oil was hydrogenated in contact with the sulphurized catalysts C (Example 1) under various processing conditions.

The results are listed in Table 5 below.

TABLE 5

|    | Experiment No.                  | 1     | 2     | 3     |
|----|---------------------------------|-------|-------|-------|
| 35 | pressure (atm)                  | 100   | 100   | 200   |
|    | temperature (°C)                | 345   | 345   | 345   |
|    | throughput (kg/l/hr)            | 0.15  | 0.25  | 0.15  |
|    | product                         |       |       |       |
| 40 | density at 20°C (g/l)           | 0.849 | 0.852 | 0.851 |
|    | viscosity at 50°C (centistokes) | 14.1  | 16.01 | 16.6  |
|    | oxygen content (ppm)            | 0     | 0     | 0     |
|    | sulphur content (ppm)           | 0.2   | 0.3   | 0.2   |
|    | nitrogen content (ppm)          | 1.0   | 2.0   | 1.0   |
| 45 | light absorption at             |       |       |       |
|    | 275 nm (DAB 7 limit 0.8)        | 10.0  | 19.8  | 1.6   |
|    | 295 nm (DAB 7 limit 0.4)        | 6.5   | 17.8  | 0.7   |
|    | 300 nm (DAB 7 limit 0.3)        | 5.8   | 15.8  | 0.6   |

These results show that the hydrogenation activity of catalyst C is so good that technical white oils of excellent quality are obtained even when operating in a single stage, the quality of said oils almost reaching that required of medicinal white oils in test 3.

To prepare a DAB 7 grade medicinal white

oil, the product obtained in experiment No. 2 in Table 5 above was subjected to a second hydrogenation stage in contact with catalyst D (Example 2) for substantial removal of all aromatics (Sulfur and nitrogen were not measured). The test results are listed in Table 6 below.

TABLE 6

|    | Experiment No.                  | 4     | 5     |
|----|---------------------------------|-------|-------|
| 65 | pressure (atm)                  | 100   | 200   |
|    | temperature (°C)                | 280   | 280   |
|    | throughput (kg/l/h)             | 0.15  | 0.15  |
|    | product                         |       |       |
| 70 | density at 20°C (g/l)           | 0.851 | 0.850 |
|    | viscosity at 50°C (centistokes) | 15.8  | 15.9  |
|    | light absorption at             |       |       |
|    | 275 nm (DAB limit 0.8)          | 0.7   | 0.3   |
|    | 295 nm (DAB limit 0.4)          | 0.24  | 0.1   |
|    | 300 nm (DAB limit 0.3)          | 0.21  | 0.1   |

Even when working at a pressure of 100 atmospheres, which is relatively low for the preparation of white oils, there is obtained a white oil which satisfies the specifications of DAB 7 for medicinal and pharmaceutical white oils. When operating at a pressure of 200 atmospheres, the light absorption results

are considerably below the limits set for pharmaceutical white oils.

## WHAT WE CLAIM IS:—

1. A process for the manufacture of a technical white oil which process comprises subjecting to catalytic hydrogenation a petro-

- leum fraction which boils in the range 200° to 550°C and which contains aromatic compounds together with nitrogen-containing, oxygen-containing and sulphur-containing compounds and which may or may not have been subjected to solvent extraction, the catalytic hydrogenation being carried out in a single stage at superatmospheric pressure and elevated temperature in the presence of a sulphurized catalyst which contains molybdenum in an amount of from 10% to 15% by weight (measured as MoO<sub>3</sub>) together with nickel and phosphoric acid and which has been prepared by impregnating a catalyst support with a solution containing Ni<sup>2+</sup> cations, MoO<sub>4</sub><sup>2-</sup> anions and PO<sub>4</sub><sup>3-</sup> anions.
2. A process for the manufacture of a medicinal white oil which process comprises subjecting to catalytic hydrogenation a petroleum fraction which boils in the range 200° to 550°C and which contains aromatic compounds together with nitrogen-containing, oxygen-containing and sulphur-containing compounds and which may or may not have been subjected to solvent extraction, the catalytic hydrogenation being carried out in two stages of which the first hydrogenation stage is carried out at superatmospheric and elevated temperature and effects hydrogenation of the nitrogen-containing, oxygen-containing and sulphur-containing compounds and a portion of the aromatic compounds and is carried out in the presence of a catalyst as defined in claim 1, and of which the second hydrogenation stage effects completion of the hydrogenation in contact with a base metal catalyst.
3. A process as claimed in claim 1 and including a stage in which the technical white oil is subsequently subjected to hydrogenation in the presence of a base metal catalyst to produce a medicinal white oil.
4. A process as claimed in any of claims 1 to 3 wherein the petroleum fraction used as starting material is a gas oil fraction boiling at from 220 to 340°C, a spindle oil fraction or other lubricating oil fraction.
5. A process as claimed in any of claims 1 to 4 wherein the petroleum fraction is hydrogenated in the presence of a catalyst containing, in the oxide state, from 3 to 6% by weight of nickel oxide, from 10 to 15% by weight of molybdenum oxide and from 3 to 6% by weight of o-phosphoric acid on an alumina-containing support.
6. A process as claimed in claim 5 wherein the support for the catalyst is made up of 95 to 100% by weight of γ-alumina and 0 to 5% by weight SiO<sub>2</sub>.
7. A process as claimed in any of claims 1 to 6 wherein the crude petroleum fraction is hydrogenated under the following conditions: a pressure of 30 to 200 atmospheres, a temperature of 250 to 370°C, a gas/oil ratio of from 0.1 to 1.0 m<sup>3</sup> of hydrogen (STP) per kilogram of oil and a space velocity of from 0.15 to 1.0 kg of oil per litre of catalyst per hour.
8. A process as claimed in claim 2 or 3 or any of claims 4 to 7 when appendent thereto wherein the catalyst used in the final hydrogenation stage is derived from the precursor
- $$\text{Ni}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}.$$
- by compression, calcination above 350°C and reduction in a stream of hydrogen.
9. A process as claimed in claim 2 or 3 or any of claims 4 to 8 when appendent thereto wherein the second hydrogenation is effected under the following conditions: a pressure of from 50 to 250 atmospheres, a temperature of from 200 to 350°C, a gas/oil ratio of from 0.1 to 1.0 m<sup>3</sup> of hydrogen (STP) per kg of oil and a space velocity of from 0.15 to 2.0 kg of oil per litre of catalyst per hour.
10. A process as claimed in claim 1 or 2 and substantially as described in either of Examples 3 and 4.
11. Technical white oils when manufactured by a process as claimed in claim 1 or in any of claims 4 to 7 or 10 appendent thereto.
12. Medicinal white oils when manufactured by a process as claimed in claim 2 or 3 or in any of claims 4 to 10 appendent thereto.
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